



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Shigeru YAMAGO et al

Serial No. : 10/523,611

For : PROCESS FOR PRODUCTION OF LIVING RADICAL POLYMERS AND  
POLYMERS

Hon. Commissioner of Patent and Trademarks

Washington, D.C. 20231

DECLARATION

Sir:

In the matter of Japanese Patent

Application No. 231,917/2002

I, Iwao Tamura, residing at c/o Tamura International Patent  
Office, 9-22, Terauchi 1-chome, Toyonaka-shi, Osaka 561-0872, JAPAN,  
who am a patent attorney solemnly and sincerely declare as follows:

1. That I understand well the Japanese and English languages.
2. That the document attached hereto is a full true and  
faithful translation into English, made by me Iwao Tamura, of the  
above Japanese patent application.
3. That I hereby declare that all statements made herein of  
my own knowledge are true and that all statements made on  
information and belief are believed to be true; and further that  
these statements were made with the knowledge that willful false  
statements and the like so made are punishable by fine or  
imprisonment, or both, under Section 1001 of Title 18 of the United  
States Code and that such willful false statements may jeopardize  
the validity of the application or any patent issued thereon.

May 16, 2007

Iwao Tamura

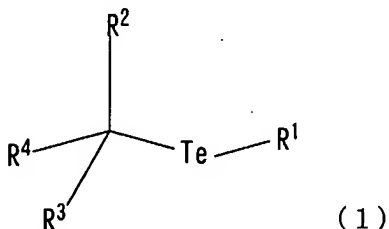


[Document Name] Specification

[Title of the Invention] ROCESS FOR PRODUCTION OF LIVING  
RADICAL POLYMERS AND POLYMERS

5 [What is claimed is]

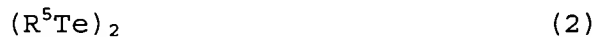
1. A process for producing a living radical polymer characterized in that a vinyl monomer is polymerized with use of a living radical polymerization initiator represented by the formula (1) and a compound represented by the formula (2)



10

wherein R<sup>1</sup> is C<sub>1</sub>-C<sub>8</sub> alkyl, aryl, substituted aryl or an aromatic heterocyclic group, R<sup>2</sup> and R<sup>3</sup> are each a hydrogen atom or C<sub>1</sub>-C<sub>8</sub> alkyl, and R<sup>4</sup> is aryl, substituted aryl, an aromatic heterocyclic group, acyl, oxycarbonyl or cyano

15



wherein R<sup>5</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl, aryl, substituted aryl or an aromatic heterocyclic group.

20

2. A living radical polymer obtainable by polymerizing a vinyl monomer with use of a living radical polymerization initiator represented by the formula (1) and a compound represented by the formula (2).

3. A mixture of a living radical polymerization initiator represented by the formula (1) and a compound represented by the formula (2).

[Detailed Description of the Invention]

5 [Technical field of the invention]

The present invention relates to a process for producing living radical polymers and the living radical polymers obtained by the process.

[Prior art]

10 Living radical polymerization is a polymerization process which is adapted for precision control of molecular structures while ensuring convenience and universal usefulness of radical polymerization, and is powerful means for preparing novel polymer materials. Georges et al has made  
15 a report on a typical example of living radical polymerization using TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) as an initiator (publication of JP-A No. 1994-199916).

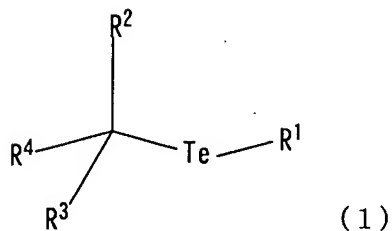
[Problems to be solved by the invention]

20 This process makes it possible to control molecular weights and molecular weight distributions, but requires a high polymerization temperature of 130°C and is difficult to use for monomers having a thermally unstable functional group. The process is also unsuited to the control of  
25 modification of terminal functional groups of high molecular weight compounds.

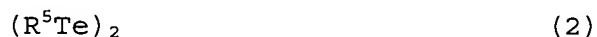
An object of the present invention is to provide a process for producing a living radical polymer by polymerizing a vinyl monomer with use of an organotellurium compound represented by the formula (1) and a compound  
 5 represented by the formula (2), the process making possible precision control of molecular weights and molecular weight distributions ( $PD=M_w/M_n$ ) under mild conditions, and the polymer.

[Means for solving the problem]

10 The present invention provides a process for producing a living radical polymer characterized in that a vinyl monomer is polymerized with use of a living radical polymerization initiator represented by the formula (1) and a compound represented by the formula (2), and the living  
 15 radical polymer obtained by the process



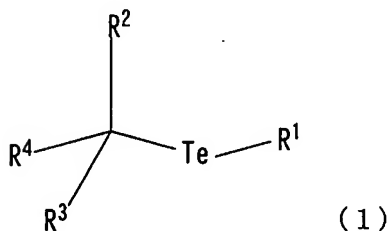
wherein  $R^1$  is  $C_1$ - $C_8$  alkyl, aryl, substituted aryl or an aromatic heterocyclic group,  $R^2$  and  $R^3$  are each a hydrogen atom or  $C_1$ - $C_8$  alkyl, and  $R^4$  is aryl, substituted aryl, an  
 20 aromatic heterocyclic group, oxycarbonyl or cyano



wherein  $R^5$  is  $C_1$ - $C_4$  alkyl, aryl, substituted aryl or an aromatic heterocyclic group.

[Embodiment of practicing the invention]

The living radical polymer of the present invention is  
 5 produced by polymerizing a vinyl monomer in the presence of a compound represented by the formula (2) using a living radical polymerization initiator represented by the formula (1)



10 wherein  $R^1$  is  $C_1$ - $C_8$  alkyl, aryl, substituted aryl or an aromatic heterocyclic group,  $R^2$  and  $R^3$  are each a hydrogen atom or  $C_1$ - $C_8$  alkyl, and  $R^4$  is aryl, substituted aryl, an aromatic heterocyclic group, oxycarbonyl or cyano  
 $(R^5Te)_2$  (2)

15 wherein  $R^5$  is  $C_1$ - $C_4$  alkyl, aryl, substituted aryl or an aromatic heterocyclic group.

The living radical polymerization initiator to be used in the present invention is a compound represented by the formula (1).

20 Examples of groups represented by  $R^1$  are as follows.

Examples of  $C_1$ - $C_8$  alkyl groups usable are straight-

chain, branched chain or cyclic alkyl groups having 1 to 8 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, cyclopropyl, n-butyl, sec-butyl, tert-butyl, cyclobutyl, n-pentyl, n-hexyl, n-heptyl and n-octyl. Preferable alkyl groups are straight-chain or branched chain alkyl groups having 1 to 4 carbon atoms. Methyl or ethyl is more preferable.

Examples of groups usable include aryl groups such as phenyl and naphthyl, substituted aryl groups such as phenyl having a substituent and naphthyl having a substituent, and aromatic heterocyclic groups such as pyridyl, furyl and thienyl. Examples of substituents of aryl groups having a substituent are a halogen atom, hydroxyl, alkoxyl, amino, nitro, cyano, carbonyl-containing groups represented by  $-COR^6$  ( $R^6 = C_1-C_8$  alkyl, aryl,  $C_1-C_8$  alkoxyl or aryloxy), sulfonyl, trifluoromethyl, etc. Preferable aryl groups are phenyl and trifluoromethyl-substituted phenyl. Preferably such substituted groups have one or two substituents at the para-position or ortho-position.

Examples of groups represented by  $R^2$  and  $R^3$  are as follows.

Examples of  $C_1-C_8$  alkyl groups usable are the same as the alkyl groups represented by  $R^1$  and given above.

Examples of groups represented by  $R^4$  are as follows.

Examples of aryl, substituted aryl, aromatic heterocyclic groups usable are the same as those groups

represented by  $R^1$  and given above.

Examples of preferred oxycarbonyl groups are those represented by  $-COOR^7$  ( $R^7 = H, C_1-C_8$  alkyl or aryl) such as carboxyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, n-butoxycarbonyl, sec-butoxycarbonyl, tert-butoxycarbonyl, n-pentoxycarbonyl and phenoxycarbonyl. Methoxycarbonyl and ethoxycarbonyl are more desirable oxycarbonyl groups.

Examples of organotellurium compounds represented by the formula (1) are as follows.

Such organotellurium compounds are preferably (methyltellanyl-methyl)benzene, (1-methyltellanyl-ethyl)benzene, (2-methyltellanyl-propyl)benzene, 1-chloro-4-(methyltellanyl-methyl)benzene, 1-hydroxy-4-(methyltellanyl-methyl)benzene, 1-methoxy-4-(methyltellanyl-methyl)benzene, 1-amino-4-(methyltellanyl-methyl)benzene, 1-nitro-4-(methyltellanyl-methyl)benzene, 1-cyano-4-(methyltellanyl-methyl)benzene, 1-methylcarbonyl-4-(methyltellanyl-methyl)benzene, 1-phenylcarbonyl-4-(methyltellanyl-methyl)benzene, 1-methoxycarbonyl-4-(methyltellanyl-methyl)benzene, 1-phenoxycarbonyl-4-(methyltellanyl-methyl)benzene, 1-sulfonyl-4-(methyltellanyl-methyl)benzene, 1-trifluoromethyl-4-(methyltellanyl-methyl)benzene, 1-chloro-4-(1-methyltellanyl-ethyl)benzene, 1-hydroxy-4-(1-methyltellanyl-ethyl)benzene, 1-methoxy-4-(1-methyltellanyl-ethyl)benzene, 1-amino-4-(1-methyltellanyl-ethyl)benzene, 1-nitro-4-(1-methyltellanyl-ethyl)benzene, 1-cyano-4-(1-methyltellanyl-ethyl)benzene.

methyltellanyl-ethyl)benzene, 1-methylcarbonyl-4-(1-  
 methyltellanyl-ethyl)benzene, 1-phenylcarbonyl-4-(1-  
 methyltellanyl-ethyl)benzene, 1-methoxycarbonyl-4-(1-  
 methyltellanyl-ethyl)benzene, 1-phenoxy carbonyl-4-(1-  
 5 methyltellanyl-ethyl)benzene, 1-sulfonyl-4-(1-methyltellanyl-  
 ethyl)benzene, 1-trifluoromethyl-4-(1-methyltellanyl-  
 ethyl)benzene, 1-chloro-4-(2-methyltellanyl-propyl)benzene,  
 1-hydroxy-4-(2-methyltellanyl-propyl)benzene, 1-methoxy-4-(2-  
 methyltellanyl-propyl)benzene, 1-amino-4-(2-methyltellanyl-  
 10 propyl)benzene, 1-nitro-4-(2-methyltellanyl-propyl)benzene,  
 1-cyano-4-(2-methyltellanyl-propyl)benzene, 1-methylcarbonyl-  
 4-(2-methyltellanyl-propyl)benzene, 1-phenylcarbonyl-4-(2-  
 methyltellanyl-propyl)benzene, 1-methoxycarbonyl-4-(2-  
 methyltellanyl-propyl)benzene, 1-phenoxy carbonyl-4-(2-  
 15 methyltellanyl-propyl)benzene, 1-sulfonyl-4-(2-  
 methyltellanyl-propyl)benzene, 1-trifluoromethyl-4-(2-  
 methyltellanyl-propyl)benzene, 2-(methyltellanyl-  
 methyl)pyridine, 2-(1-methyltellanyl-ethyl)pyridine, 2-(2-  
 methyltellanyl-propyl)pyridine, methyl 2-methyltellanyl-  
 20 ethanate, methyl 2-methyltellanyl-propionate, methyl 2-  
 methyltellanyl-2-methylpropionate, ethyl 2-methyltellanyl-  
 ethanate, ethyl 2-methyltellanyl-propionate, ethyl 2-  
 methyltellanyl-2-methylpropionate, 2-  
 methyltellanylacetonitrile, 2-methyltellanyl-propionitrile,  
 25 2-methyl-2-methyltellanyl-propionitrile, (phenyltellanyl-  
 methyl)benzene, (1-phenyltellanyl-ethyl)benzene, (2-

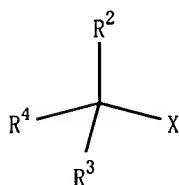


phenyltellanyl-propyl)benzene, etc.

Preferable are (methyltellanyl-methyl)benzene, (1-methyltellanyl-ethyl)benzene, (2-methyltellanyl-propyl)benzene, methyl 2-methyltellanyl-2-methylpropionate,  
 5 ethyl 2-methyltellanyl-2-methylpropionate, 2-methyltellanyl-propionitrile, 2-methyl-2-methyltellanylpropionitrile.

The living radical polymerization initiator represented by the formula (1) can be prepared by reacting a compound of the formula (3), a compound of the formula (4) and metallic  
 10 tellurium.

Examples of compounds represented by the formula (3) are as follows.



(3)

wherein  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are as defined above, and X is a halogen  
 15 atom.

Examples of groups represented by  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are as given above.

Examples of groups represented by X can be a halogen atom such as fluorine, chlorine, bromine or iodine. Chlorine  
 20 and bromine are preferable.

Examples of compounds usable are benzyl chloride, benzyl bromide, 1-chloro-1-phenylethane, 1-bromo-1-phenylethane, 2-chloro-2-phenylpropane, 2-bromo-2-

phenylpropane, p-chlorobenzyl chloride, p-hydroxybenzyl  
 chloride, p-methoxybenzyl chloride, p-aminobenzyl chloride,  
 p-nitrobenzyl chloride, p-cyanobenzyl chloride, p-  
 methylcarbonylbenzyl chloride, phenylcarbonylbenzyl chloride,  
 5 p-methoxycarbonylbenzyl chloride, p-phenoxy carbonylbenzyl  
 chloride, p-sulfonylbenzyl chloride, p-trifluoromethylbenzyl  
 chloride, 1-chloro-1-(p-chlorophenyl)ethane, 1-bromo-1-(p-  
 chlorophenyl)ethane, 1-chloro-1-(p-hydroxyphenyl)ethane, 1-  
 bromo-1-(p-hydroxyphenyl)-ethane, 1-chloro-1-(p-  
 10 methoxyphenyl)ethane, 1-bromo-1-(p-methoxyphenyl)ethane, 1-  
 chloro-1-(p-aminophenyl)ethane, 1-bromo-1-(p-  
 aminophenyl)ethane, 1-chloro-1-(p-nitrophenyl)ethane, 1-  
 bromo-1-(p-nitrophenyl)ethane, 1-chloro-1-(p-  
 cyanophenyl)ethane, 1-bromo-1-(p-cyanophenyl)ethane, 1-  
 15 chloro-1-(p-methylcarbonylphenyl)ethane, 1-bromo-1-(p-  
 methylcarbonylphenyl)ethane, 1-chloro-1-(p-  
 phenylcarbonylphenyl)ethane, 1-bromo-1-(p-  
 phenylcarbonylphenyl)-ethane, 1-chloro-1-(p-  
 methoxycarbonylphenyl)ethane, 1-bromo-1-(p-  
 20 methoxycarbonylphenyl)ethane, 1-chloro-1-(p-  
 phenoxy carbonylphenyl)-ethane, 1-bromo-1-(p-  
 phenoxy carbonylphenyl)ethane, 1-chloro-1-(p-  
 sulfonylphenyl)ethane, 1-bromo-1-(p-sulfonylphenyl)ethane, 1-  
 chloro-1-(p-trifluoromethylphenyl)ethane, 1-bromo-1-(p-  
 25 trifluoromethylphenyl)ethane, 2-chloro-2-(p-  
 chlorophenyl)propane, 2-bromo-2-(p-chlorophenyl)propane, 2-

chloro-2-(p-hydroxyphenyl)-propane, 2-bromo-2-(p-  
 hydroxyphenyl)propane, 2-chloro-2-(p-methoxyphenyl)propane,  
 2-bromo-2-(p-methoxyphenyl)propane, 2-chloro-2-(p-  
 aminophenyl)propane, 2-bromo-2-(p-aminophenyl)propane,  
 5 chloro-2-(p-nitrophenyl)propane, 2-bromo-2-(p-nitrophenyl)-  
 propane, 2-chloro-2-(p-cyanophenyl)propane, 2-bromo-2-(p-  
 cyanophenyl)propane, 2-chloro-2-(p-  
 methylcarbonylphenyl)propane, 2-bromo-2-(p-  
 methylcarbonylphenyl)propane, 2-chloro-2-(p-  
 10 phenylcarbonylphenyl)propane, 2-bromo-2-(p-  
 phenylcarbonylphenyl)-propane, 2-chloro-2-(p-  
 methoxycarbonylphenyl)propane, 2-bromo-2-(p-  
 methoxycarbonylphenyl)propane, 2-chloro-2-(p-  
 phenoxy carbonylphenyl)propane, 2-bromo-2-(p-  
 15 phenoxy carbonylphenyl)propane, 2-chloro-2-(p-  
 sulfonylphenyl)propane, 2-bromo-2-(p-sulfonylphenyl)propane,  
 2-chloro-2-(p-trifluoromethylphenyl)propane, 2-bromo-2-(p-  
 trifluoromethylphenyl)propane, 2-(chloromethyl)pyridine, 2-  
 (bromomethyl)pyridine, 2-(1-chloroethyl)pyridine, 2-(1-  
 20 bromoethyl)pyridine, 2-(2-chloropropyl)pyridine, 2-(2-  
 bromopropyl)pyridine, methyl 2-chloroethanoate, methyl 2-  
 bromoethanoate, methyl 2-chloropropionate, methyl 2-  
 bromoethanoate, methyl 2-chloro-2-methylpropionate, methyl 2-  
 bromo-2-methylpropionate, ethyl 2-chloroethanoate, ethyl 2-  
 25 bromoethanoate, ethyl 2-chloropropionate, ethyl 2-  
 bromoethanoate, ethyl 2-chloro-2-ethylpropionate, ethyl 2-

bromo-2-ethylpropionate, 2-chloroacetonitrile, 2-bromoacetonitrile, 2-chloropropionitrile, 2-bromopropionitrile, 2-chloro-2-methylpropionitrile, 2-bromo-2-methylpropionitrile, etc.

5           Examples of compounds represented by the formula (4) are as follows.



wherein  $R^1$  is as defined above, M is an alkali metal, alkaline earth metal or copper atom, and m is 1 when M is an alkali  
10 metal, m is 2 when M is an alkaline earth metal, or m is 1 or 2 when M is a copper atom.

Examples of groups represented by  $R^1$  are as given above.

Examples of metals represented by M are lithium, sodium, potassium and like alkali metals, magnesium, calcium  
15 and like alkaline earth metals, and copper. Lithium is desirable.

In case that M is magnesium, the compound (4) may either be  $Mg(R^1)_2$  or a compound represented by  $MgX$  (X is a halogen atom) which is a Grignard reagent. Chlorine and  
20 bromine are preferable.

Examples of compounds usable are methyllithium, ethyllithium, n-butyllithium, phenyllithium, p-chlorophenyllithium, p-methoxyphenyllithium, p-nitro phenyllithium, etc. Methyllithium, ethyllithium and  
25 phenyllithium are preferable.

Next, a detailed description will be given of the process

for preparing the compound.

5       Metallic tellurium is suspended in a solvent. Examples of solvents usable are dimethylformamide (DMF), tetrahydrofuran (THF) and like polar solvents, toluene, xylene and like aromatic solvents, hexane and like aliphatic hydrocarbons, dialkyl ethers and like ethers, etc. THF is preferable. The amount of solvent to be used, which is suitably adjusted, is 1 to 10 ml, preferably 7 to 8 ml, per gram of metallic tellurium.

10       A compound (4) is slowly added dropwise to the suspension, followed by stirring. The reaction time differs with the reaction temperature and pressure and is usually 5 minutes to 24 hours, preferably 10 minutes to 2 hours. The reaction temperature is  $-20^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ , preferably  $15^{\circ}\text{C}$  to  $40^{\circ}\text{C}$ , more preferably room temperature. The reaction is conducted usually under atmospheric pressure, but may be conducted at increased pressure or in a vacuum.

20       Next, a compound (3) is added to the reaction mixture, followed by stirring. The reaction time differs with the reaction temperature and pressure and is usually 5 minutes to 24 hours, preferably 10 minutes to 2 hours. The reaction temperature is  $-20^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ , preferably  $15^{\circ}\text{C}$  to  $40^{\circ}\text{C}$ , more preferably room temperature. The reaction is conducted usually under atmospheric pressure, but may be conducted at increased pressure or in a vacuum.

25       The proportions of the compound (3) and compound (4) to

metallic tellurium are 0.5 to 1.5 moles of the compound (3) and 0.5 to 1.5 moles of the compound (4), preferably 0.8 to 1.2 moles of the compound (3) and 0.8 to 1.2 moles of the compound (4), per mole of metallic tellurium.

5        After the completion of the reaction, the solvent is concentrated, and the desired compound is isolated and purified. Although the method of purification can be determined suitably depending on the compound, usually vacuum distillation or recrystallization is preferable.

10        The vinyl monomer to be used in the present invention is not particularly limited insofar as the monomer can be subjected to radical polymerization. Examples of vinyl monomers usable are methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 15 octyl (meth)acrylate, lauryl (meth)acrylate and like (meth)acrylic acid esters, cyclohexyl (meth)acrylate, methylcyclohexyl (meth)acrylate, isobornyl (meth)acrylate, cyclododecyl (meth)acrylate and like cycloalkyl-containing unsaturated monomers, (meth)acrylic acid, maleic acid, 20 fumaric acid, itaconic acid, citraconic acid, crotonic acid, maleic anhydride and like carboxyl-containing unsaturated monomers, N,N-dimethylaminopropyl (meth)acrylamide, N,N-dimethylaminoethyl (meth)acrylamide, 2-(dimethylamino)ethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate and 25 like unsaturated monomers containing a tertiary amine, N-2-hydroxy-3-acryloyloxypropyl-N,N,N-trimethylammonium chloride,

N-methacryloylaminoethyl-N,N,N-dimethylbenzylammonium chloride and like unsaturated monomers containing quaternary ammonium base, glycidyl (meth)acrylate and like epoxy- containing unsaturated monomers, styrene,  $\alpha$ -methylstyrene, 4-  
 5 methylstyrene, 2-methylstyrene, 3-methylstyrene, 4-methoxystyrene, 2-hydroxymethylstyrene, 2-chlorostyrene, 4-chlorostyrene, 2,4-dichlorostyrene, 1-vinylnaphthalene, divinylbenzene, p-styrenesulfonic acid or an alkali metal salt thereof (sodium salt or potassium salt, etc.) and like  
 10 aromatic unsaturated monomers, 2-vinylthiophene, N-methyl-2-vinylpyrrole and like unsaturated monomers containing a heterocyclic ring, N-vinylformaldehyde, N-vinylacetamide and like vinylamides, 1-hexene, 1-octene, 1-decene and like  $\alpha$ -olefins, vinyl acetate, hydroxyethyl (meth)acrylate,  
 15 acrylonitrile, acrylamide, N,N-dimethylacrylamide, vinyl chloride, etc.

Preferable among these are (meth)acrylic acid ester monomers, unsaturated monomers containing a tertiary amine, styrene type monomers, acrylamide, and N,N-  
 20 dimethylacrylamide.

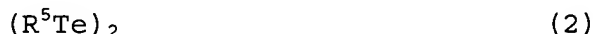
Examples of preferable (meth)acrylic acid ester monomers are methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate and butyl (meth)acrylate. Especially preferable are methyl (meth)acrylate and butyl  
 25 (meth)acrylate.

Examples of preferable unsaturated monomers containing

a tertiary amine are N,N-dimethylaminoethyl(meth)acrylamide and 2-(dimethylamino)ethyl(meth)acrylate.

Examples of preferable styrene type monomers are styrene,  $\alpha$ -methylstyrene, o-methylstyrene, p-methylstyrene, p-methoxystyrene, p-t-butylstyrene, p-n-butylstyrene p-chlorostyrene, and p-styrenesulfonic acid or an alkali metal salt thereof (sodium salt or potassium salt, etc.). More preferable are styrene, p-methoxystyrene and p-chlorostyrene. The term "(meth)acrylic acid" refers collectively to "acrylic acid" and "methacrylic acid."

Examples of compounds represented by the formula (2) and useful for the present invention are as follows



wherein  $R^5$  is  $C_1$ - $C_4$  alkyl, aryl, substituted aryl or an aromatic heterocyclic group.

Examples of groups represented by  $R^5$  are as follows.

Examples of  $C_1$ - $C_4$  alkyl groups usable are straight-chain, branched chain or cyclic alkyl groups having 1 to 4 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, cyclopropyl, n-butyl, sec-butyl, tert-butyl and cyclobutyl. Preferable alkyl groups are methyl or ethyl.

Examples of aryl, substituted aryl, aromatic heterocyclic groups usable are the same as those groups represented by  $R^1$  and given above.

More specific examples of compounds represented by the formula (2) are dimethyl ditelluride, diethyl ditelluride,



di-n-propyl ditelluride, diisopropyl ditelluride,  
dicyclopropyl ditelluride, di-n-butyl ditelluride, di-sec-  
butyl ditelluride, di-tert-butyl telluride, dicyclobutyl  
telluride, diphenyl ditelluride, bis(p-methoxyphenyl)  
5 ditelluride, bis(p-aminophenyl) ditelluride, bis(p-  
nitrophenyl) ditelluride, bis(p-cyanophenyl) ditelluride,  
bis(p-sulfonylphenyl) ditelluride, dinaphthyl ditelluride,  
dipyridyl ditelluride, etc.

Next, a detailed description will be given of the process  
10 for preparing the compound.

Metallic tellurium is suspended in a solvent. Examples  
of solvents usable are dimethylformamide (DMF),  
tetrahydrofuran (THF) and like polar solvents, toluene,  
xylene and like aromatic solvents, hexane and like aliphatic  
15 hydrocarbons, dialkyl ethers and like ethers. THF is  
preferable among these. The organic solvent is used usually  
in an amount of 5 to 10 ml, preferably 7 to 8 ml, per gram of  
metallic tellurium although the amount is suitably adjustable.

The compound represented by the formula (4) is slowly  
20 added dropwise to the suspension, followed by stirring. The  
reaction time is usually 5 minutes to 24 hours, preferably 10  
minutes to 2 hours, although varying with the reaction  
temperature and pressure. The reaction temperature is  $-20^{\circ}\text{C}$   
to  $80^{\circ}\text{C}$ , preferably  $15^{\circ}\text{C}$  to  $40^{\circ}\text{C}$ , more preferably room  
25 temperature. The reaction is conducted usually at atmospheric  
pressure, but an increased or reduced pressure is usable.

Subsequently, water (which may be neutral water such as saline solution, alkali water such as aqueous solution of ammonium chloride, or acid water such as aqueous solution of hydrochloric acid) is added to the reaction mixture, followed  
5 by stirring. Although varying with the reaction temperature or pressure, the reaction time is usually 5 minutes to 24 hours, preferably 10 minutes to 2 hours. The reaction temperature is  $-20^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ , preferably  $15^{\circ}\text{C}$  to  $40^{\circ}\text{C}$ , more preferably room temperature. The reaction is conducted  
10 usually at atmospheric pressure, but an increased or reduced pressure is usable.

Metallic tellurium and the compound of the formula (4) are used in such a ratio that 0.5 to 1.5 moles, preferably 0.8 to 1.2 moles, of the compound of the formula (4) is used  
15 per mole of metallic tellurium.

After the completion of the reaction, the solvent is concentrated, and the desired product is isolated from the concentrate and purified. Although the compound can be purified by a suitably selected method, vacuum distillation  
20 or reprecipitation purification is usually desirable.

Specifically stated, the living radical polymer of the present invention is produced by the process to be described below.

A vinyl monomer, a living radical polymerization,  
25 initiator represented by the formula (1) and a compound represented by the formula (2) are mixed together in a

container having its inside air replaced by an inert gas. At this time, the initiator represented by the formula (1) and the compound of the formula (2) may be mixed together by stirring as the first step, followed by the second step of adding the vinyl monomer to the mixture. Examples of inert gases usable at this time are nitrogen, argon, helium, etc., among which argon and nitrogen are preferred. Nitrogen is especially preferred.

Although the vinyl monomer and the initiator represented by the formula (1) are used in amounts which are suitably adjusted depending on the molecular weight and molecular weight distribution of the living radical polymer to be obtained, usually 5 to 10,000 moles, preferably 50 to 5,000 moles, of the vinyl monomer is used per mole of the initiator represented by the formula (1).

The living radical polymerization initiator represented by the formula (1) and the compound represented by the formula (2) are used in the ratio of usually 0.5 to 100 moles, preferably 1 to 10 moles, especially preferably 1 to 5 moles, of the compound of the formula (2) per mole of the initiator of the formula (1).

The polymerization reaction is conducted usually in the absence of solvent, while an organic solvent generally in use for radical polymerization may be used. Examples of solvents usable are benzene, toluene, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetone, chloroform, carbon

tetrachloride, tetrahydrofuran (THF), ethyl acetate, trifluoromethylbenzene, etc. The amount of the solvent to be used is adjusted suitably. For example, 0.01 to 1 ml, preferably 0.05 to 0.5 ml, of the solvent is used per gram of  
5 the vinyl monomer.

Next, the mixture is then stirred. The reaction temperature and the reaction time may be adjusted suitably in accordance with the molecular weight or molecular weight distribution of the living radical polymer to be obtained.  
10 The mixture is stirred usually at 60 to 150°C for 5 to 100 hours, preferably at 80 to 120°C for 10 to 30 hours. The reaction is conducted usually under atmospheric pressure, but may be conducted at increased pressure or in a vacuum..

After the completion of the reaction, the solvent used  
15 and the remaining monomer are removed in a vacuum to take out the desired polymer, or the desired product is isolated by re-precipitation using a solvent wherein the product is insoluble. The reaction mixture can be treated by any method insofar as it causes no problem to the desired product.

20 The living radical polymerization initiator of the present invention is adapted for excellent control of molecular weights and molecular weight distributions under very mild conditions.

The living radical polymer to be obtained by the  
25 invention is adjustable in molecular weight according to the reaction time and the amount of organotellurium compounds,

and can be 500 to 1,000,000 in number average molecular weight. The invention is especially suitable for producing living radical polymers having a number average molecular weight of 1,000 to 50,000.

5       The living radical polymer to be obtained by the invention is controlled to 1.05 to 1.50 in molecular weight distribution ( $PD = M_w/M_n$ ). The molecular weight distribution is controllable to a narrower range of 1.05 to 1.30, a further narrower range of 1.05 to 1.20, a still narrower  
10 range of 1.05 to 1.15.

It has been found that the living radical polymer of the present invention has a terminal group which is an alkyl, aryl, substituted aryl, aromatic heterocyclic group, oxycarbonyl or cyano derived from the organotellurium  
15 compound and a growth terminal which is highly reactive tellurium. Accordingly, the organotellurium compound used for radical polymerization makes it easier to convert the terminal group to other functional group than in the case of the living radical polymer obtained by conventional living  
20 radical polymerization. The living radical polymer obtained according to the invention is therefore usable as a macro living radical polymerization initiator (macroinitiator).

A-B diblock copolymers such as methyl methacrylate-styrene, A-B-A triblock copolymers such as methyl  
25 methacrylate-styrene-methyl methacrylate and A-B-C triblock copolymers such as methyl methacrylate-styrene-butyl acrylate

can be obtained using a macro living radical polymerization initiator of the invention. This is attributable to the fact that the vinyl monomers of various different types are controllable by the living radical polymerization initiator  
5 and the ditellurium compound of the invention, and also to the fact that highly reactive tellurium is present at the growth terminal of the living radical polymer obtained with use of the living radical polymerization initiator.

Stated more specifically, block copolymers are prepared  
10 by the processes to be described below.

For preparing A-B diblock copolymers such as methyl methacrylate-styrene copolymer, methyl methacrylate, a living radical polymerization initiator represented by the formula (1) and a compound represented by the formula (2) are mixed  
15 together first as in the process described above for preparing a living radical polymer to obtain poly(methyl methacrylate), and subsequently mixing styrene with the polymer to obtain methyl methacrylate-styrene copolymer.

A-B-A triblock copolymers and A-B-C triblock copolymers  
20 can be produced, for example, by preparing an A-B diblock copolymer by the above process and thereafter mixing a vinyl monomer (A) or vinyl monomer (C) with the copolymer to obtain the A-B-A or A-B-C triblock copolymer.

The preparation of each block may be followed directly  
25 by the subsequent reaction for the next block, or the subsequent reaction for the next block may be initiated after

the purification of the product resulting from the completion of the first reaction. The block copolymer can be isolated by a usual method.

## 5 [Examples]

The present invention will be described below in detail with reference to Examples, but is not limited thereto in any way. In Examples and Comparative Examples, properties were determined by the following methods.

### 10 (1) Identification of organotellurium compounds and living radical polymers

The organotellurium compound was identified based on the results of  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, IR and MS analyses. The molecular weight and molecular weight distribution of the living  
15 radical polymer were determined using GPC (gel permeation chromatography). The measuring instruments used are as follows.

$^1\text{H}$ -NMR : Varian Gemini 2000 (300MHz for  $^1\text{H}$ ), JEOL JNM-A400 (400MHz for  $^1\text{H}$ )

20  $^{13}\text{C}$ -NMR : Varian Gemini 2000, JEOL JNM-A400

IR : Shimadzu FTIR-8200 ( $\text{cm}^{-1}$ )

MS(HRMS) : JEOL JMS-300

Molecular weight and molecular weight distribution : liquid chromatography Shimadzu LC-10 (column : Shodex K-804L + K-  
25 805L, polystyrene standard : TOSOH TSK Standard, polymethyl methacrylate standard : Shodex Standard M-75)

## Preparation Example 1

Preparation of (1-methyltellanyl-ethyl)benzene

A 6.38 g quantity (50 mmoles) of metallic tellurium  
5 [product of Aldrich, brand name: Tellurium (-40 mesh)] was  
suspended in 50 ml of THF, and 52.9 ml (1.04 M diethyl ether  
solution, 55 mmoles) of methyllithium (product of Kanto  
Chemical Co., Ltd., diethyl ether solution) was slowly added  
dropwise to the suspension at room temperature (for 10  
10 minutes). The reaction mixture was stirred until the metallic  
tellurium disappeared completely (for 20 minutes). To the  
reaction mixture was added 11.0 g (60 mmoles) of (1-  
bromoethyl)benzene at room temperature, followed by stirring  
for 2 hours. After the completion of reaction, the solvent  
15 was concentrated in a vacuum, followed by vacuum distillation  
to give 8.66 g of yellow oil (70% in yield).

IR, HRMS,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR analyses indicated that  
the product was (1-methyltellanyl-ethyl)benzene.

IR(neat,  $\text{cm}^{-1}$ ) 1599, 1493, 1451, 1375, 1219, 1140, 830, 760,  
20 696, 577

HRMS (EI)  $m/z$ : Calcd for  $\text{C}_9\text{H}_{12}\text{Te}(\text{M})^+$ , 250.0001; Found 250.0001

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ) 1.78 (s, 3H,  $\text{TeCH}_3$ ), 1.90 (d,  $J=7.2\text{Hz}$ ,  
3H), 4.57 (q,  $J=7.2\text{Hz}$ , 1H,  $\text{CHTe}$ ), 7.08-7.32 (m, 5H)

$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ) -18.94, 18.30, 23.89, 126.17, 126.80,  
25 128.30, 145.79

## Preparation Example 2



Preparation of ethyl-2-methyl-2-methyltellanyl-propionate

The same procedure as in Preparation Example 1 was performed with the exception of using 10.7 g (55 mmol) of ethyl-2-bromo-isobutyrate in place of (1-bromoethyl)benzene to obtain 6.53 g (51% in yield) of yellow oil.

IR, HRMS,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR analyses indicated that the product was ethyl-2-methyl-2-methyltellanyl-propionate.

IR(neat,  $\text{cm}^{-1}$ ) 1700, 1466, 1385, 1269, 1146, 1111, 1028

HRMS (EI) m/z: Calcd for  $\text{C}_7\text{H}_{14}\text{O}_2\text{Te}(\text{M})^+$ , 260.0056; Found

260.0053

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ) 1.27 (t,  $J=6.9\text{Hz}$ , 3H), 1.74 (s, 6H), 2.15 (s, 3H,  $\text{TeCH}_3$ ), 4.16 (q,  $J=7.2\text{Hz}$ , 2H)

$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ) -17.38, 13.89, 23.42, 27.93, 60.80, 176.75

Preparation Example 3 (dimethyl ditelluride)

A 3.19 g quantity (25 mmol) of metallic tellurium (the same as above) was suspended in 25 ml of THF, and 25 ml (28.5 mmol) of methyllithium (the same as above) was added slowly to the suspension at  $0^\circ\text{C}$  (over a period of 10 minutes).

The reaction mixture was stirred until the metallic tellurium disappeared completely (for 10 minutes). To the resulting reaction mixture was added 20 ml of a solution of ammonium chloride at room temperature, followed by stirring for 1 hour. The organic layer was separated off, and the aqueous layer was subjected to extraction with diethyl ether 3 times. The organic layers were collected, dried over anhydrous sodium

sulfate and concentrated in a vacuum, affording 2.69 g (9.4 mmoles, yield 75%) of blackish purple oil.

The product was found to be dimethyl ditelluride by MS (HRMS) and  $^1\text{H-NMR}$ .

5 HRMS(EI)m/z : Calcd for  $\text{C}_2\text{H}_6\text{Te}_2(\text{M})^+$ , 289.8594; Found 289.8593  
 $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ) 2.67 (s, 6H)

#### Preparation Example 4 (diphenyl ditelluride)

A 3.19 g quantity (25 mmoles) of metallic tellurium (the same as above) was suspended in 25 ml of THF, and 15.8  
 10 ml (28.5 mmoles) of phenyllithium [product of Aldrich; 1.8M-cyclohexane/ether (70:30) solution] was added slowly to the suspension at  $0^\circ\text{C}$  (over a period of 10 minutes). The reaction mixture was stirred until the metallic tellurium disappeared completely (for 10 minutes). To the resulting  
 15 reaction mixture was added 20 ml of a solution of ammonium chloride at room temperature, followed by stirring for 1 hour. The organic layer was separated off, and the aqueous layer was subjected to extraction with diethyl ether 3 times. The organic layers were collected, dried over anhydrous sodium  
 20 sulfate and concentrated in a vacuum, affording 3.48 g (8.5 mmoles, yield 68%) of blackish purple oil.

The product was found to be diphenyl ditelluride by MS (HRMS) and  $^1\text{H-NMR}$ .

#### Examples 1 to 4

#### 25 Preparation of poly(methyl methacrylate)

Along with 24.8 mg (0.10 mmole) of the (1-

methyltellanyl-ethyl)benzene prepared in Preparation Example  
 1, methyl methacrylate [stabilized with hydroquinone (HQ)]  
 and a solution of the dimethyl ditelluride prepared in  
 Preparation Example 3 were placed in the ratio listed in  
 5 Table 1 into a glove box with the inside air replaced by  
 nitrogen, followed by stirring. After the completion of the  
 reaction, the reaction mixture was dissolved in 5 ml of  
 chloroform, and the solution was then poured into 250 ml of  
 hexane which was being stirred. The resulting polymer  
 10 precipitate was collected by suction filtration and dried to  
 obtain polymethacrylate.

Table 1 shows the result of GPC analysis [with  
 reference to the molecular weight of an authentic sample of  
 poly(methyl methacrylate)].

15

Table 1

<u>Ex.</u>	<u>methyl methacrylate</u>	<u>dimethyl ditelluride</u>	<u>reaction condition</u>	<u>yield (%)</u>	<u>Mn</u>	<u>PD</u>
1	1.01 g (10 mmol)	28.5 mg (0.10 mmol)	80 °C 13 h	92	9700	1.18
2	2.02 g (20 mmol)	28.5 mg (0.10 mmol)	80 °C 13 h	83	16100	1.14
3	5.05 g (50 mmol)	57.0 mg (0.20 mmol)	80 °C 18 h	79	36300	1.18
4	10.10 g (100 mmol)	57.0 mg (0.20 mmol)	80 °C 24 h	83	79400	1.14

## Comparative Example 1

Preparation of poly(methyl methacrylate)

20

Poly(methyl methacrylate) was prepared in the same

manner as in Example 1 except that no dimethyl ditelluride was used (67% in yield).

GPC analysis [with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)] revealed Mn  
5 8100 and PD=1.77.

A comparison between Example 1 and Comparative Example 1 indicates that when dimethyl telluride was used as a compound represented by the formula (2), a living radical polymer of narrower molecular weight distribution (PD value  
10 closer to 1) is obtained.

#### Example 5

##### Preparation of poly(methyl methacrylate)

A 25.8 mg quantity (0.10 mmole) of the ethyl-2-methyl-2-methyltellanyl-propionate prepared in Preparation Example 2,  
15 1.01 g (10 mmoles) of methyl methacrylate and a solution of 28.5 mg (0.10 mmole) of the dimethyl ditelluride prepared in Preparation Example 3 were stirred at 80° C for 13 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture  
20 was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 0.85 g (yield 84%) of polymethacrylate.

25 GPC analysis [with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)] revealed Mn

8200 and PD=1.16.

#### Example 6

##### Preparation of poly(ethyl methacrylate)

A 25.8 mg quantity (0.10 mmole) of the ethyl-2-methyl-  
5 2-methyltellanyl-propionate prepared in Preparation Example 2,  
1.14 g (10 mmoles) of ethyl methacrylate (stabilized with HQ)  
and a solution of 28.5 mg (0.10 mmole) of the dimethyl  
ditelluride prepared in Preparation Example 3 were stirred at  
105° C for 2 hours within a glove box having its inside air  
10 replaced by nitrogen. After the completion of the reaction,  
the reaction mixture was dissolved in 5 ml of chloroform, and  
the solution was thereafter poured into 250 ml of hexane  
being stirred. The resulting polymer precipitate was  
collected by suction filtration and dried, affording 1.11 g  
15 (yield 97%) of polymethacrylate.

GPC analysis [with reference to the molecular weight of  
an authentic sample of poly(methyl methacrylate)] revealed Mn  
10600 and PD=1.12.

#### Example 7

##### 20 Preparation of poly(2-hydroxyethyl methacrylate)

In 1 ml of N,N-dimethylformamide (DMF) were dissolved  
25.8 mg (0.10 mmole) of the ethyl-2-methyl-2-methyltellanyl-  
propionate prepared in Preparation Example 2, 1.30 g (10  
mmoles) of 2-hydroxyethyl methacrylate [stabilized with  
25 hydroquinone methyl ether (MEHQ)] and 28.5 mg (0.10 mmole) of  
the dimethyl ditelluride prepared in Preparation Example 3 in

a glove box having its inside air replaced by nitrogen. The solution was stirred at 80° C for 8 hours. After the completion of the reaction, the solvent was removed by distillation in a vacuum, affording 1.26 g (yield 97%) of poly(2-hydroxyethyl methacrylate).

GPC analysis [with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)] revealed Mn 22300 and PD=1.27.

#### Example 8

##### 10 Preparation of polystyrene

A 24.8 mg quantity (0.10 mmole) of the (1-methyltellanyl-ethyl)benzene prepared in Preparation Example 1, 1.04 g (10 mmoles) of styrene and a solution of 28.5 mg (0.10 mmole) of the dimethyl ditelluride prepared in Preparation Example 3 were stirred at 120° C for 1.4 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 1.01 g (yield 97%) of polystyrene.

GPC analysis (with reference to the molecular weight of an authentic sample of polystyrene) revealed Mn 9000 and PD=1.18.

#### Example 9

### Preparation of polystyrene

A 24.8 mg quantity (0.10 mmole) of the (1-methyltellanyl-ethyl)benzene prepared in Preparation Example 1, 1.04 g (10 mmoles) of styrene and a solution of 40.9 mg (0.10 mmole) of the diphenyl ditelluride prepared in Preparation Example 4 were stirred at 120° C for 14 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 0.99 g (yield 95%) of polystyrene.

GPC analysis (with reference to the molecular weight of an authentic sample of polystyrene) revealed Mn 9200 and PD=1.13.

### Example 10

### Preparation of poly(methyl methacrylate-b-styrene) diblock polymer

A 1.001 g quantity (10 mmoles) of methyl methacrylate, 24.8 mg (0.10 mmole) of the (1-methyltellanyl-ethyl)benzene prepared in Preparation Example 1 and 28.5 mg (0.10 mmole) of the dimethyl ditelluride prepared in Preparation Example 3 were reacted at 100° C for 24 hours in a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of

deuteriochloroform, and the solution was thereafter poured into 300 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 0.765 g (yield 86%) of poly(methyl methacrylate).

5 GPC analysis revealed Mn 8500 and PD=1.12.

Next, 425 mg (0.05 mmole) of the poly(methyl methacrylate) (used as a macroinitiator) obtained above and 520 mg (5 mmoles) of styrene were reacted at 100° C for 24 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 300 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 0.5353 g (yield 57%) of poly(methyl methacrylate-b-polystyrene) diblock polymer. GPC  
10 analysis revealed Mn 18700 and PD=1.18.

[Effects of the invention]

The invention provides a process for preparing living radical polymers which realizes precision control of molecular weights and molecular weight distributions under mild conditions. The living radical polymers obtained by the polymerization process of the invention readily permit  
20 conversion of terminal groups to other functional groups, are useful for preparing macromonomers and useful as crosslinking sites and are usable as compatibilizing agents and as  
25 materials for block polymers.

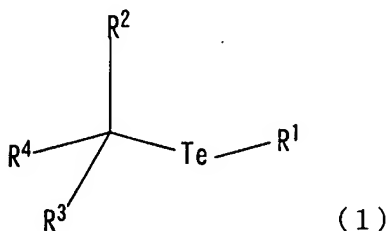


[Document Name] Abstract

[Abstract]

[Problem] The present invention provides a process for producing a living radical polymer by polymerizing a vinyl monomer with use of an organotellurium compound represented by the formula (1) and a compound represented by the formula (2), the process making possible precision control of molecular weights and molecular weight distributions (PD=Mw/Mn) under mild conditions, and the polymer.

[Solving means] A process for producing a living radical polymer characterized in that a vinyl monomer is polymerized with use of a living radical polymerization initiator represented by the formula (1) and a compound represented by the formula (2), and the living radical polymer obtained by the process



wherein  $R^1$  is  $C_1$ - $C_8$  alkyl, aryl, substituted aryl or an aromatic heterocyclic group,  $R^2$  and  $R^3$  are each a hydrogen atom or  $C_1$ - $C_8$  alkyl, and  $R^4$  is aryl, substituted aryl, an aromatic heterocyclic group, oxycarbonyl or cyano



wherein  $R^5$  is  $C_1$ - $C_4$  alkyl, aryl, substituted aryl or an aromatic heterocyclic group.